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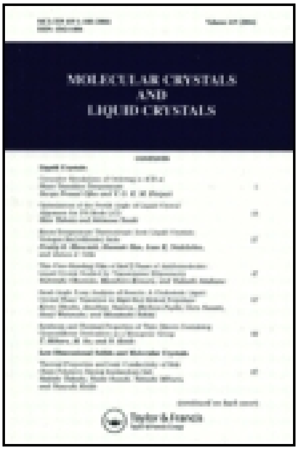

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Shinya Yoshioka [a], Naoko Okamoto [a] & Shuichi Kinoshita [a]

[a] Graduate School of Frontier Biosciences, Osaka University, Suita City, Osaka, Japan

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Spatial Pattern Formation Induced by Rapid Temperature Change in a Cholesteric Liquid Crystal

Shinya Yoshioka
Naoko Okamoto
Shuichi Kinoshita
Graduate School of Frontier Biosciences, Osaka University, Suita City, Osaka, Japan

We report an experimental study on a transient spatial pattern formation of a cholesteric liquid crystal, cholesteryl oleyl carbonate, induced by rapid temperature change. The spatial pattern like a network is found to be induced when the temperature is increased faster than a constant rate of 0.5 mK/s. We have measured the optical transmittance of the liquid crystal continuously during the pattern formation process and have found that the component corresponding to the network clearly appears in addition to the selective reflection of the helical structure. The observed spatial pattern is discussed in relation to the spectral shape of the transmittance.

Keywords: cholesteric liquid crystal; nonequilibrium states; spatial pattern formation; temperature change

INTRODUCTION

Recently, pattern formation or self-organization processes under nonequilibrium conditions have been attracting a lot of research interest. For example, Belousov-Zhabotinsky reaction is one of the most investigated systems from physical, chemical, biological and engineering points of view. The interfacial instability of the unidirectional solidification under rapid crystal growth is another good example. Cholesteric liquid crystals attract our attention in a different way.

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Address correspondence to Shinya Yoshioka, Graduate School of Frontier Biosciences, Osaka University, Yamadaoka 1–3, Suita City, Osaka 565–0871, Japan. E-mail: syoshi@fbs.osaka-u.ac.jp

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They have the helical structure of the director orientation, whose helix pitch is largely dependent on temperature and pressure. In fact, some liquid crystals are known to have a surprisingly large temperature coefficient of the pitch such as $1/p\ \mathrm{d}p/\mathrm{d}T \sim 100\ \mathrm{deg}^{-1}$, where p and T are the helix pitch and absolute temperature, respectively [1]. It is natural that the following fundamental questions arise regarding the cholesteric liquid crystals having a seemingly equilibrated structure: What will happen, if the temperature is changed so rapidly? How do they reconstruct the helical structure having the pitch preferable to that new temperature? The large temperature coefficient means that the liquid crystal has to drastically change its structure. Thus, it is probable that somewhat different behavior should be induced. We have started the present study to answer the above questions and have found, for the first time, that very peculiar spatial pattern suddenly appears when the rate of the temperature change exceeds a certain value.

EXPERIMENTAL

A sample employed in the present study was a simple cholesteric liquid crystal of a small molecular weight, cholesteryl oleyl carbonate, which shows smectic to cholesteric and cholesteric to isotropic phase transition at 17 and 34°C, respectively. The liquid crystal was purchased from Tokyo Kasei Kogyo and was used without further purification. The sample was held between two parallel glass plates which were spaced by inserting the spheres of $20\,\mu$m in diameter (Sekisui Chemical). After the cell was filled with the liquid crystal by capillary action, the planar texture was obtained by slight displacement of the glass plates to each other. The sample cell was supported between two brass plates which was temperature-controlled within 0.01°C by a temperature controller (Techno Seven Model C522). To give the temperature change, two Peltier elements were attached to both sides of the sample cell to avoid thermal convection. The brass plates and Peltier elements had a hole in a center to serve to the optical measurements. A thermistor was attached to the lateral side of the glass plates to monitor the sample temperature.

The white light from a Xenon lamp was first circularly polarized by passing a Fresnel rhomb and irradiated the sample. The reflected pattern was observed by an Olympus BX-50 fluorescent microscope equipped with an Olympus DP70 CCD camera. A part of the transmitted light was collected by an optical fiber and spectrally analyzed by a spectrometer (USB2000, Ocean Optics). The spectroscopic measurements were continuously performed during

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the pattern formation process. The transmission spectrum was obtained by dividing the observed spectrum by that of isotropic phase at higher temperature.

RESULTS AND ANALYSES

First we have examined the temperature dependence of the helix pitch. Figure 1(a)–(e) show the transmission spectrum when the sample is heated slowly at a constant rate of 0.25 mK/s. A dip corresponding to a selective reflection is clearly observed in the transmission spectrum. The center wavelength of the dip λ_{p} is related to p by the formula, $\lambda_{\mathrm{p}} = n\ p$, where n is the average refractive index. The dip gradually shifts to a shorter wavelength with temperature increase and the width becomes slightly narrower. These spectral shapes are almost the same as those obtained under thermal equilibrium conditions. As shown in Figure 2(a), the helix pitch is quite sensitive to the temperature change and, correspondingly, the liquid crystal changes the color from red to blue even within the range of 0.5 degree. The width of the dip, $\Delta\lambda$, which is obtained by fitting a spectrum using a Gaussian function, $\exp(-(\lambda-\lambda_p)^2/\Delta\lambda^2)$, shows similar temperature dependence as in Figure 2(b). This is because the width is also proportional to $p\ \Delta n$, where Δn is the difference of the refractive indices corresponding to the two principal axes of the molecule.

Under a much higher heating rate, a peculiar network appears on the uniform texture. Figure 3 shows the observed texture during a heating process at a rate of 10 mK/s. As the time elapses, the network becomes vivid and then changes into a lot of black "grains" locating on the intersecting points of the network. The grains grow slowly and gradually merge to form larger grains. The long-time behavior of the spatial pattern is more peculiar. After the sample was given the temperature rise of 0.3°C at a rate 5 mK/s for 60 seconds, the network structure was observed for a day while the temperature was kept constant. It is found that those grains grow further to be called "regions" and, after some regions become larger and others disappear, the uniform layer is finally recovered.

When the temperature is increased at a rate of 0.25 mK/s, the uniform texture just gradually changes its color without any spatial pattern. We have examined various rates of temperature increase and noticed that a threshold seems to be present around 0.5 mK/s for the peculiar pattern formation to occur. The sizes of network and grains are typically 20–40 microns when they appear and are not so sensitive to the rate of temperature increase, but sensitive to the

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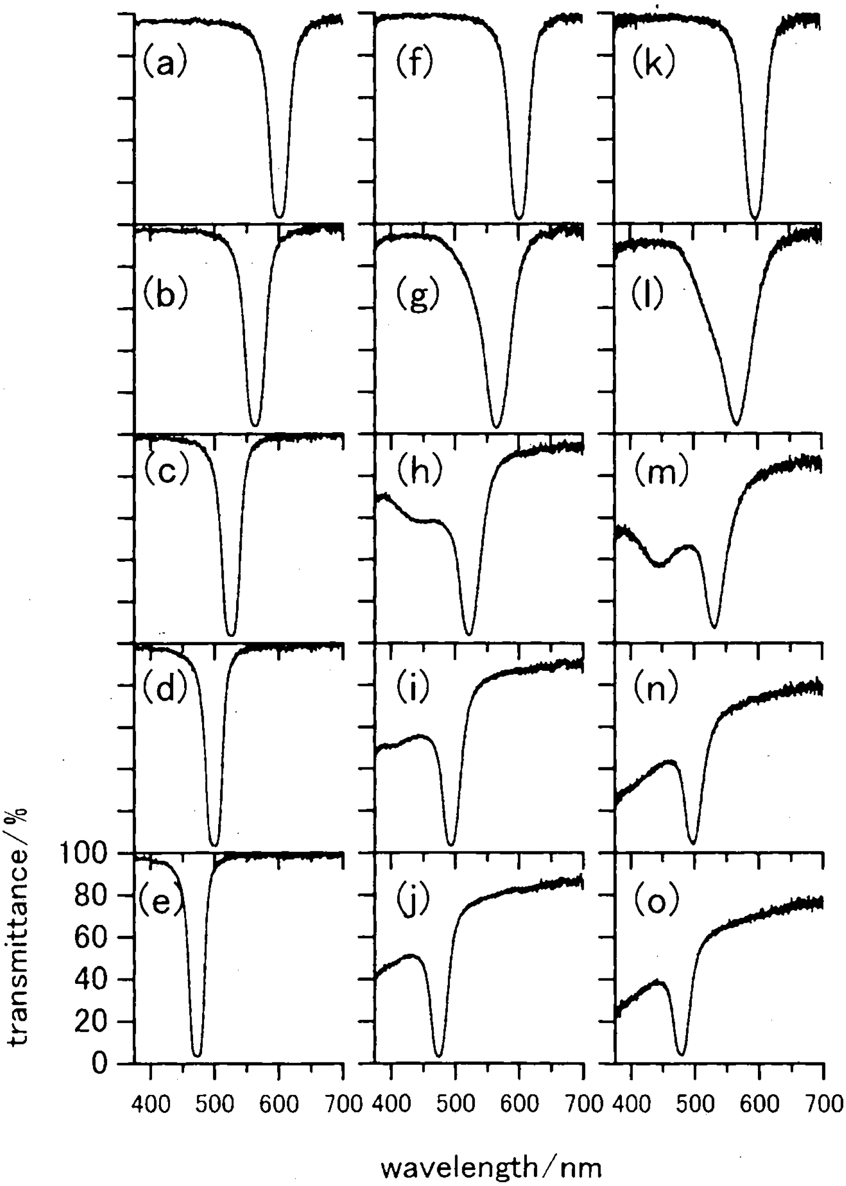

FIGURE 1 Transmittance of the liquid crystal at three different rates of temperature increase; (a)–(e) for 0.25 mK/s, (f)–(j) for 0.67 mK/s and (k)–(o) for 10 mK/s. Temperatures are 22.23, 22.31, 22.43, 22.51, 22.59°C for (a)–(e), 22.23, 22.31, 22.39, 22.47, 22.55°C for (f)–(j), 22.23, 22.35, 22.47, 22.59, 22.67°C for (k)–(o), respectively.

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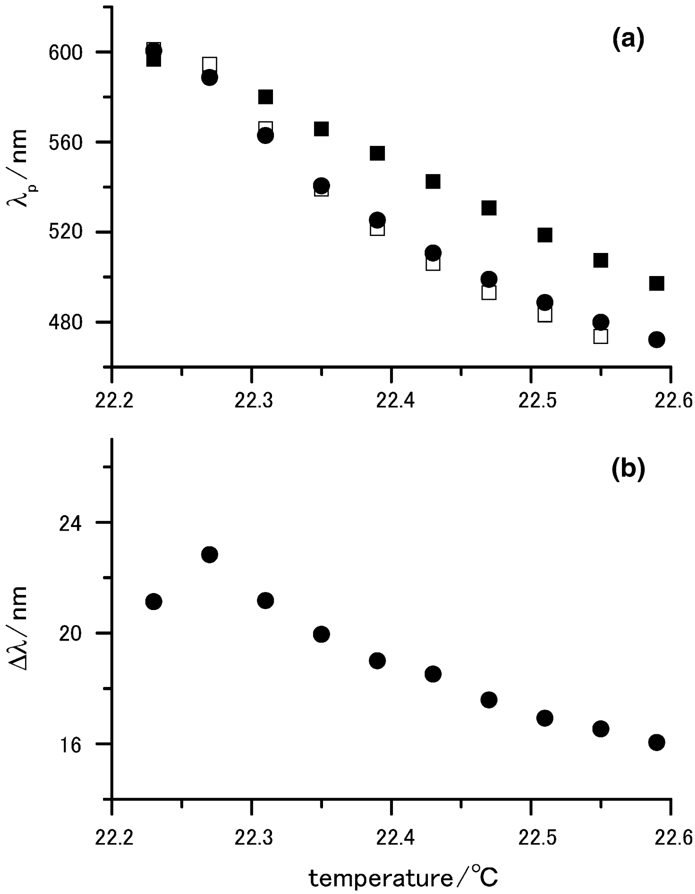

FIGURE 2 (a) Center wavelength of the dip in transmittance plotted against temperature for three increase rates, 0.25 mK/s (closed circle), 0.67 mK (open square) and 10 mK/s (closed square). The width, $\Delta\lambda$, is also shown in (b) for a rate 0.25 mK/s, where $\Delta\lambda$ is obtained by a fitting procedure assuming a Gaussian spectral shape of $\exp(-(\lambda - \lambda_p)^2/\Delta\lambda^2)$.

thickness of the sample cell: The size becomes smaller when a thinner sample cell is used.

In order to investigate the pattern formation process more clearly, we have observed the time course of the transmittance by a multichannel spectrometer. The results, shown in Figures 1(f)–(j) and (k)–(o) for the two different rates, respectively, are now very different from the case under the thermal equilibrium conditions. Besides the sharp dip owing to the selective reflection, the second component

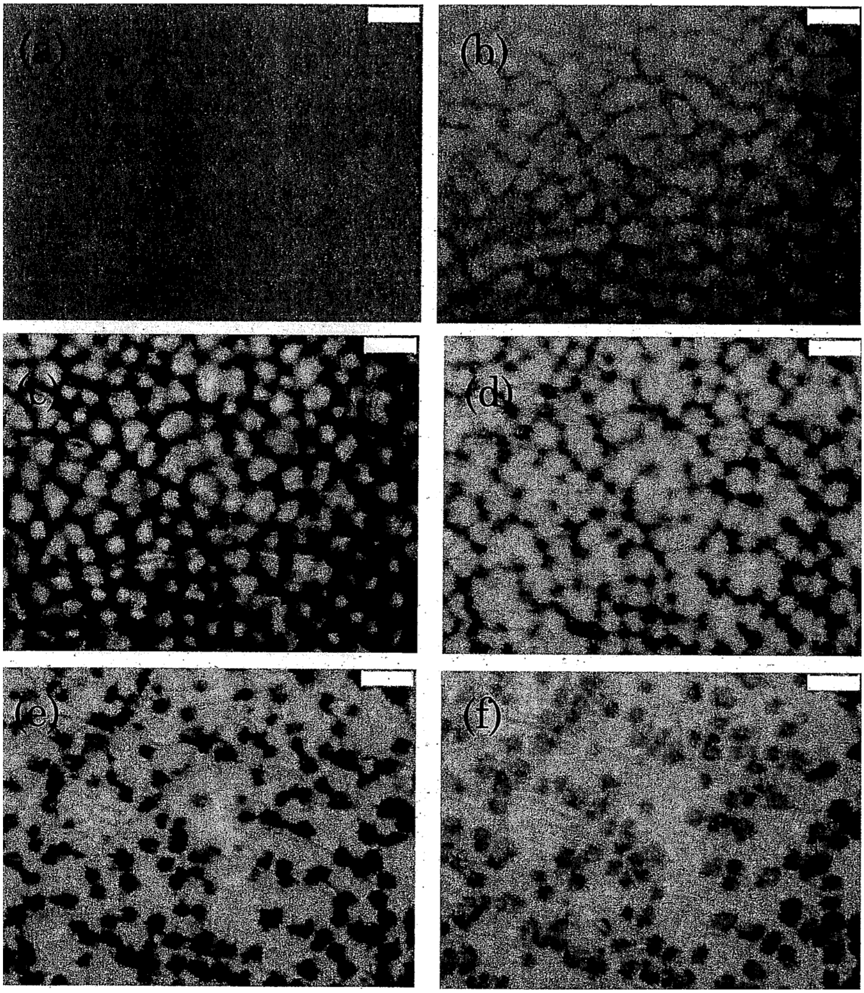

FIGURE 3 The observed spatial pattern of the liquid crystal under temperature increase of a rate 10 mK/s. Temperatures are (a): 22.23, (b): 22.43, (c): 22.53, (d): 22.63, (e): 22.73 and (f): 22.83°C. The scale bar shows 50 μm.

appears first as a broadening of the dip shown in Figures 1(g) and (i). Then, the new component rapidly shifts to a shorter wavelength and forms a broad but well-defined dip (Figs. 1(h) and (m)). It further shifts to a shorter wavelength, becoming very broad, and eventually goes out of the observable spectral range so that only the tail can be seen. We have compared the center wavelengths of the sharp dip for three rates in Figure 2(a). For slower two rates, the temperature

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dependence is almost similar to each other. On the other hand, for the rate 10 mK/s, the selective reflection is observed in a longer wavelength, implying the helix pitch cannot follow the temperature increase.

DISCUSSION

It has been reported that the helical structure of the cholesteric liquid crystals is deformed from the planar texture when they are subjected to an external field. In particular, under a magnetic and an electric field, which is applied along the helical axis, the two-dimensional cellular pattern is induced in cholesteric liquid crystals [2,3]. These phenomena have been interpreted by the instability of a sinusoidal undulation which minimizes the free energy under an external field [4–6]. Since the observed pattern is somewhat similar to the previously reported patterns, it is likely that the similar instability of the undulation triggers the pattern formation process. However, the model of the simple sinusoidal undulation fails to explain the observed spectral shapes having two separates dips in transmittance. Those spectra rather indicate that a complicated structure is realized inside the pattern. Since the second component of the spectra, which is thought to correspond to the part of the network and/or grains, appears in a shorter wavelength, it may be possible to say that the structure inside the network has a shorter helix pitch or highly tilted layers. Further, the rapid shift and broadening of the component mean the structure becomes quite inhomogeneous and/or or irregular.

To answer the fundamental question why the spatial pattern is induced by the rapid temperature increase, it is helpful to recall an instability in a liquid-crystal interface during the crystal growth. When a liquid, for example, succinonitrile, is cooled sufficiently fast, the flat interface becomes unstable to result in the formation of a dendrite pattern [7,8]. It is possible to say that this instability is a manifestation of the nature originally prepared in the material under thermally nonequilibrium conditions and that the pattern appears through the instability during the rapid cooing process which forces the material to crystallize fast. The cholesteric liquid crystal has an intrinsic character to form the metastable sinusoidal undulation as the theoretical calculation proves. The present study reveals the modulated state is realized not only by an external field but also by the thermally nonequilibrium conditions as the appearance of definite separate regions having different helix pitches. Further investigations are now in progress.

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